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A procedure of separation and preconcentration for titanium determination in seawater samples by ICP-OES

Sérgio A. Rocha[a,b] **and Sérgio L. C. Ferreira**[a]

[a] Universidade Federal da Bahia, Instituto de QuímicaGrupo de Pesquisa em Química Analítica, Salvador, Bahia, Brasil 40170-290

[b] Universidade Federal do Recôncavo da Bahia, Centro de Formação de Professores, Amargosa, Bahia, Brasil 40300-000

Abstract

In the present paper, a procedure for separation, preconcentration and determination of trace amounts of titanium in seawater samples by using inductively coupled plasma optical emission spectrometry (ICP-OES) has been proposed. It is based on the complexation of titanium(IV) ions by 4-(2-thiazolylazo)-orcinol (TAO) and hydroxylamine chlorhydrate reagents and its sorption onto activated carbon. Parameters such as: pH effect on the complexation and sorption, TAO amount, hidroxylamine chlorhydrate amount, shaking time, mass of activated carbon, desorption of titanium from activated carbon, sample volume, effect of other ions and analytical features were studied. Results demonstrated that the titanium(IV) ions, within the pH range from 3.8 to 7.0, as TAO complex, has been quantitatively recovered (90-110%) onto activated carbon. The TAO amount required was 1.0 mg and the hidroxylamine chlorhydrate amount was 20.0 mg.The shaking time required for sorption was 5 min by using 100 mg of activated carbon. A successfully desorption of titanium for its determination by ICP-OES was achieved by heating the loaded activated carbon with 3 mol L^{-1} nitric acid solution because is strongly adsorved the complex. The precision of the procedure, calculated as the relative standard deviations were 4.7 and 2.5% for titanium concentrations 1.0 and 2.5 $\mu g\ L^{-1}$**,** respectively**.** The limit of detection was 0.01 $\mu g\ L^{-1}$, for a sample volume of 400 mL, considering the achieved enrichment factor of 80. The method was tolerant to other ions usually present in seawater samples. The procedure was applied to determine this element in seawater samples collected in beaches of the cities of Arembepe and Salvador, Bahia-Brazil.

Keywords: Titanium; Seawater; ICP-OES; Preconcentration; Activated carbon.

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1. Introduction

Titanium determination in seawater is not an easy task, considering the low concentration of titanium in these samples, due to the hydrolyze of the titanila cation (TiO^{2+}) and the alkaline pH of seawater. The determination of very low concentrations of dissolved titanium is therefore a challenging task. Inductively coupled plasma optical emission spectrometry (ICP-OES) [1-5] is one of the analytical techniques more convenient for determination of trace amounts of titanium. However, for titanium determination in seawater samples a preconcentration step is also necessary.

This paper proposes an analytical procedure for preconcentration and determination of titanium in seawater samples by ICP-OES, after chelation with 4-(2-thiazolylazo)-orcinol and hydroxylamine chlorhydrate reagents and its sorption onto activated carbon.

The thiazolylazo dyes have been utilized in Analytical Chemystry. The 4-(2-thiazolylazo)-orcinol is a complexing reagent, which was first synthesized long time ago [6] and was proposed as metalocromic indicator for cupper, cobalt, nickel, lead e cadmium. Afterwards, TAO was studied as reagent spectrophotometric for trace metals [7].

Many procedures of preconcentration can be found literature employing a variety of materials, such as amberlite XAD [8], chelating resins [9,10], ion-exchangers [11,12], silica gel [13], polyurethane foam [14] or activated carbon [15-24].

Activated carbon is an adsorbent widely used. The use of actived carbon provides some advantages. Firstly, very high concentration factors in different matrices [19-22]. Secondly, alkali and alkaline earth elements are not retained [22]. In our laboratory, it was used in preconcentration procedures for molybdenum determination in geological samples and seawater [20] and for vanadium and copper determination in seawater by ICP-OES [21]. In both cases a successfully desorption of the analites was achieved by heating the loaded activated carbon with nitric acid solutions.

2. Experimental

2.1. Apparatus

A sequential inductively coupled atomic emission plasma spectrometer Applied Research Laboratories model 3410 minitorch with an IBM PC-AT computer was used. The emission intensity measurements were made under the conditions shown in Table 1. The calibration graph

(0-0.200 μg mL^{-1}) for titanium was built with solutions prepared from 1 mg mL^{-1} stock solution. The ionic emission line Ti II 334.941 nm was used.

Table 1. Operating parameters for the inductively coupled plasma spectrometer

Incident output power	650 W
Reflected power	< 5W
Nebulizer	Glass, Meinhard
Plasma gas flow rate	7.5 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}
Aerosol carrier gas flow	0.8 mL min^{-1}
Solution uptake rate	2.5 L min^{-1}
Signal integration time	5s
Integration for determination (sample replicates)	3

A 300 ANALYSER pH meter was used to measure the pH values. A VKS-100 Mechanical Shaker 100 cpm was used to shake the solutions.

2.2. Reagents

All reagents were of analytical grade unless otherwise stated. Double distilled water was used to prepare all solutions. The nitric acid and hydrochloric acid were of Suprapur quality (Merck). Laboratory glassware was kept overnight in a 10%(v/v) nitric acid solution. Before use the glassware was rinsed with deionized water and dried in a dust free environment.

Titanium solution 10.0 μg mL^{-1} was prepared by diluting a 1000 μg mL^{-1} titanium solution (Merck) using a 1%(v/v) hydrochloric acid solution.

TAO solution 0.01%(m/v) was prepared by dissolving 0.05 g of TAO (SIGMA-Aldrich) in 500 mL of ethanol.

Hidroxylamine chlorhydrate solution 1%(m/v) was prepared by dissolving 1.00 g of hidroxylamine chlorhydrate (MERCK) in 100 mL of desionated water.

2.3. Sample Collection

Seawater samples were collected in Polytetrafluoroethylene (PTFE) flasks from surface of aqueous systems, in different places of the cities of Arembepe and Salvador, Bahia, Brazil in February 2004. The samples were filtered through a cellulose membrane (Millipore) of 0.45 μm pore size. Samples were analysed with and without addition of 1.00 μg of titanium to perform a recovery test.

2.4. Enrichment Procedure

In stoppered flasks it was added a sample volume of 400 mL of seawater containing titanium(IV) ions (in the range 0.004 – 10 μg). Then it was added 2 mL of 1% (m/v) hidroxylamine chlorhydrate solution. pH values within the range from 4.5 to 5.5 were adjusted with acetate buffer. Then it was added 5 mL of 0.02% (m/v) TAO solution. After shaking it was added a mass of 100 mg of activated carbon and the mixture was shaken for 5 min. The system was then filtered under vacuum through a cellulose membrane (Millipore) of 0.45 μm pore size set on a glass crucible. The filtered residue of activated carbon was transferred to a glass flask and was treated with 5 mL of 3 mol. L^{-1} nitric acid solution in a heating plate 40°C for 10 min for quantitative desorption. Alternatives similars have been used [20,21]. The residue was filtered in a paper filter and the filtrate was collected into a 5 mL calibrated flask.

The titanium solution was taken to determine this element by Inductively Coupled Plasma Optical Emission Spectrometry.

3. Results and Discussion

3.1. Performance of procedure

The analytical parameters as pH, shaking time, activated carbon amount, hidroxylamine chlorhydrate amount and TAO amount were optimised by using the univariate method for maximum sensitivity of the titanium determination.

The results of pH effect demonstrated that the titanium recovery was quantitative (> 90 %) and constant in the pH range of 3.8 to 7.0. Results in Fig.1 were obtained by controlling the pH with chloridric acid-glycine buffer and acetate buffer and sodium hydroxide solution and ammonia-ammonium chloride buffer. In the proposed procedure, a pH range of 4.5 to 5.5 has been recommended, considering the buffer index of acetate buffer.

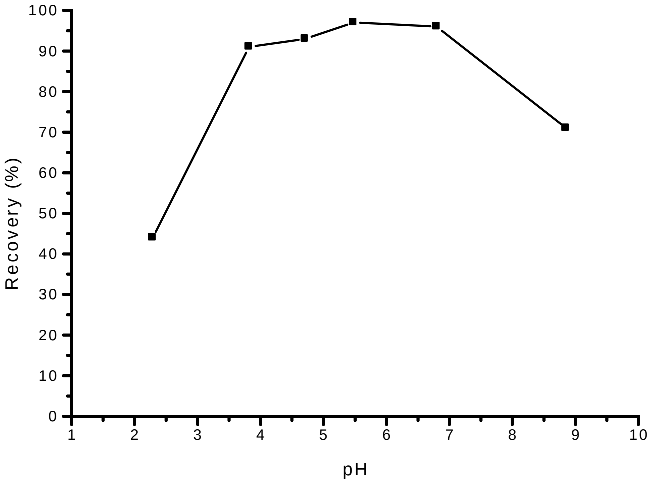

Fig 1. pH effect on the titanium sorption

The shaking time required for quantitative sorption of the TAO and its titanium complex depends on the amount of activated carbon, TAO amount and of the processed sample volume. Results demonstrated that for a solution volume of 400 mL containing 10 μg of titanium (IV) ions, 1.00 mg of TAO and an activated carbon mass of 100 mg, the shaking time required for quantitative sorption is 5 min. It can be seen in the Fig.2. The proposed procedure recommends a time shaking of 5 min.

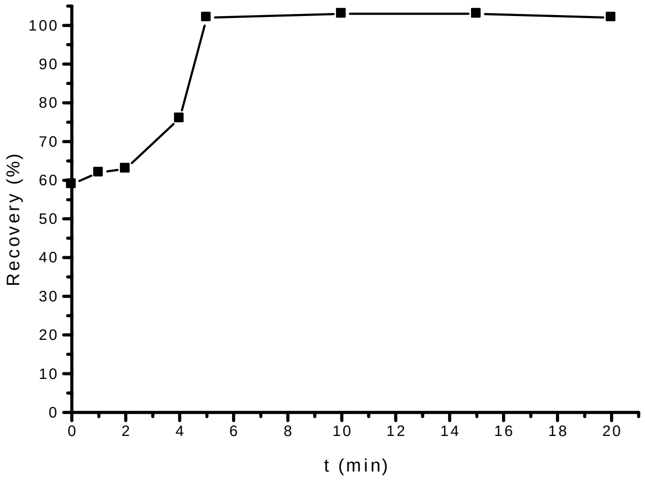

Fig.2 Shaking time on the titanium sorption

In order to determine TAO amount, 400 mL of a solution containing 10 µg of titanium (IV) ions and TAO amounts within the range from 0.04 mg to 5.00 mg were tested keeping a constant amount of activated carbon of 100 mg. It was found that the titanium recovery was quantitative (>95%) even for 1.00 mg of TAO.

The experiment showed that the Ti(IV)-TAO system is not recovery quantitative (< 90%) in the absence of hidroxylamine chlorhydrate. As the titanium(IV) is not reduced by hidroxylamine chlorhydrate [25] suggest that this salt takes part in the complex formation. A ternary Ti(IV):2-(2-thiazolylazo)-p-cresol (TAC) :$(NH_2OH)_x$ complex has been reported [17] which take believe in this supposition.

Nitric and hydrochloric acids solutions were tested for back extraction of titanium from activated carbon. Results demonstrated that 5.0 mL of 3 mol.L^{-1} nitric acid can be used for a quantitative elution. The presence TAO was not observed in the eluent during back extraction process. Recovery data are shown in Table 2.

Table 2. Effect of eluent type on the recovery

Extraction solution	Concentration	Recovery*, %
HCl	3 mol. L^{-1}	91 ± 2
HNO_3	3 mol. L^{-1}	100 ± 2

∗ At 95% confidence level (N=3)
Extraction solutions volume: 5.0 mL
Titanium(IV) concentration: 25 µg L^{-1}

Activated carbon mass: 100 mg.
TAO mass: 1.0 mg.
Shaking time: 5 min.

3.2. Analytical features

The precision of the procedure, calculated as the relative standard deviation (N=8) of the concentrations determined were 4.7 and 2.5% for titanium concentrations 1.0 and 2.5 µg L^{-1}**,** respectively.

The detection limit (LOD) defined as the concentration of titanium that gives a response equivalent to three times the standard deviation of blank (n= 30), was found to be 0.01 µg L^{-1}, for a sample volume of 400 mL. The quantification limit was calculated as the concentration that gives a response equivalent to ten times the S.D. of the blank (n=30), and define the lower limit of the range. The quantification limit (LOQ) calculated was 0.03 µg L^{-1}.

3.2. Selectivity of the proposed procedure

In order to determine the tolerance of other ions in the proposed procedure, solutions containing titanium and other ions, were prepared and the developed procedure was applied. The following ions in the concentrations in the brackets: Na^{1+} (1.5 g L^{-1}), K^{1+} (1.0 g L^{-1}), Ca^{2+} and Mg^{2+} (25 mg L^{-1}), Mo^{6+} (250 μg L^{-1}), Pb^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+},Mn^{2+} and Cu^{2+} (25 μg L^{-1}), NO_3^{1-} (0.1 g L^{-1}) and Cl^{1-} (1.5 g L^{-1}) do not interfere in the titanium determination (2.5 μg L^{-1}). These data are not the limits. Other concentrations could be tested. The interference was defined as loss or enhancement of analytical signal by 10 %. These results demonstrated that the procedure could be applied for titanium determination in seawater samples, considering the proportions among titanium and other tested ions.

3.3. Application

The results presented in Table 3 correspond to the titanium determination in seawater samples.

Besides the advantages of separation, the determination of titanium in seawater samples was achieved with preconcentration of titanium within the range from 0.04 to 0.15 μg L^{-1}. A large sample volume of 400 mL was used. This volume was selected based on preliminary experiments. In the procedure was employed 4.00 mg of TAO for guaranteeing a maximum sorption of titanium in presence of other ions.

Seawater samples were analysed and results are presented in Table 3. Values presented good recovery and are similar to those reported for seawater in literature [26].

4. Conclusions

The titanium complexation with TAO and hydroxylamine chlorhydrate and adsorption in activated carbon was efficient to separate and preconcentrate it from seawater. A high enrichment factor, simplicity of procedures and the fact that complexation takes place at low pH are real advantages of this procedure.

Achieved results for titanium in seawater samples collected in beaches of the cities of Arembepe and Salvador, Bahia-Brazil, were in good agreement with other reported data from literature.

Table 3. Determination and recovery of titanium in seawaters

Simple	Added titanium (μg L^{-1})	Achieved Titanium (μg L^{-1})	Recovery (%)
Seawater *Arembepe*	0	0.07 ± 0.02	100
	0.25	0.32 ± 0.02	
Seawater *Stella Mares*	0	0.07 ± 0.02	96
	0.25	0.31 ± 0.02	
Seawater *Ondina*	0	0.04 ± 0.02	104
	0.25	0.30 ± 0.02	
Seawater *Ipiranga*	0	< LD	96
	0.25	0.24 ± 0.03	
Seawater *Rio Vermelho*	0	0.15 ± 0.02	96
	0.25	0.39 ± 0.02	

∗ At 95% confidence level (N=3).
Sample volume: 400 mL

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Sérgio A. Rocha **Corresponding Author**	Dr., Proffesor at the Universidade Federal da Bahia, Brasil. **Address:** Universidade Federal da Bahia, Instituto de Química Grupo de Pesquisa em Química Analítica Salvador, Bahia, Brasil 40170-290 **Address:** Universidade Federal do Recôncavo da Bahia, Centro de Formação de Professores, Amargosa, Bahia, Brasil 40300-000 **Phone:** +55-75-38341823 **Fax:** +55-71-32374117 **E-mail:** srocha@ufba.br
Sérgio L. C. Ferreira	Dr., Proffesor at the Universidade Federal da Bahia, Brasil. **Address:** Universidade Federal da Bahia, Instituto de Química Grupo de Pesquisa em Química Analítica Salvador, Bahia, Brasil 40170-290 **Phone:** +55-71- 3235166 **Fax:** +55-71-32374117 **E-mail:** slcf@ufba.br